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Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/.1.2150827

Publication date:
2006

Document Version
Publisher's PDF, also known as Version of record

The effect of surface relaxation on the N_2 dissociation rate on stepped Ru: A transition state theory study

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(Received 25 August 2005; accepted 18 November 2005; published online 10 January 2006)

[DOI: 10.1063/1.2150827]

The dissociation of N_2 on stepped Ru is the rate limiting step in the industrial synthesis of ammonia on Ru catalysts (see Refs. 1–4). In a preceding paper,[5] we have examined the effect of tunneling on the reaction rate for N_2 on a stepped Ru surface with (0001) terraces. The positions of the surface atoms were frozen, in order to reduce the computational effort. The strong tunneling effect found in previous model calculations[6–11] is not found. In contrast, the tunneling effect was very small above room temperature. The thermal rate constant obtained from harmonic transition state theory (TST) therefore agrees very well with the accurate quantum-mechanical result. In this note we further examine the accuracy of the harmonic TST rate constant and consider the effect of surface motion. Different models to take the effect of surface motion in account are employed. The best theoretical result for the thermal sticking coefficient, which is proportional to the thermal rate constant, is then compared with experiment.

Density-functional theory (DFT) calculations are performed to localize the transition state and to determine energies and vibrational frequencies at the transition state. Technical details are the same as in Ref. 5, except that the present work also includes relaxations of the Ru atoms in the topmost two layers. The transition state of N_2 dissociation is localized by constraining the N–N distance and relaxing both the other nitrogen degrees of freedom and the positions of the Ru atoms in the topmost two layers. By varying the N–N distance we localized the saddle point. The calculated barrier height for a relaxed surface is 0.65 eV. It should be noted that this barrier is higher than the one reported by Logadóttir and Nørskov.[1] They used the same (4×2) unit cell and the same relaxed surface model. The difference is mainly due to the more accurate localization of the saddle point in the present work.

The relaxation of the surface has a considerable effect on the barrier height, lowering it from 1.0 to 0.65 eV. Therefore, it is obvious that surface degrees of freedom cannot be neglected. In principle, harmonic TST would require that all relaxed degrees of freedom are included in to the dynamical treatment. This requires lots of computer time but does not necessarily change results. Thus we include only selected atoms in the dynamical treatment.

The expression for the thermal rate constants k in transition state theory is given as

$$k=\frac{k_BT}{2\pi\hbar}\frac{Q^{\ddagger}}{Q_{\text{reactants}}}e^{-\Delta E/k_BT}, \tag{1}$$

where ΔE is the vibrationally adiabatic barrier height and $Q^{\ddagger}$ and $Q_{\text{reactants}}$ are the partition functions of the activated complex and reactants (per unit volume), respectively. ΔE, $Q^{\ddagger}$, and $Q_{\text{reactants}}$ are defined according to the specific reduced dimensional model employed. Here, the harmonic approximation is used to evaluate ΔE and the partition functions. The thermal rate constant k is related to the sticking coefficient S according to

$$S=\sqrt{\frac{2\pi m}{k_BT}}n_{\text{active}}k, \tag{2}$$

where m is mass of a N_2 molecule, and n_{active} the density of active sites on the surface. For n_{active} we use the value estimated by Logadóttir and Nørskov ($n_{\text{active}}\approx1.57\times10^{17}$ m^{-2}).[1]

The simplest approximation to include the motion of the surface atoms into the rate constant is to calculate the barrier height and the vibrational harmonic frequencies of N_2 at the transition state on a relaxed surface but neglect the vibrations of the surface atoms. Here, we call this model the "relaxed/N_2 model." This type of modeling is frequently used in the literature. To investigate the role of surface vibrations a more advanced model is needed. In a "relaxed/N_2+2Ru" model the vibrations of two-step Ru atoms next to the upper N atom are included, see Fig. 1. Due to the interaction between a dissociating N_2 molecule and the surface, the Ru atoms at the step relax upwards compared to the clean surface positions. In the relaxed/N_2+2Ru model we consider the motion of both Ru atoms in all three dimensions. Thus, the vibrational motion at the transition state involves six nitrogen and six ruthenium degrees of freedom. The harmonic frequencies for the different models are given in Table I. For the N_2+2Ru model, modes 1–5 and the mode corresponding to the imaginary frequency mainly involve motion of the nitrogen atoms,

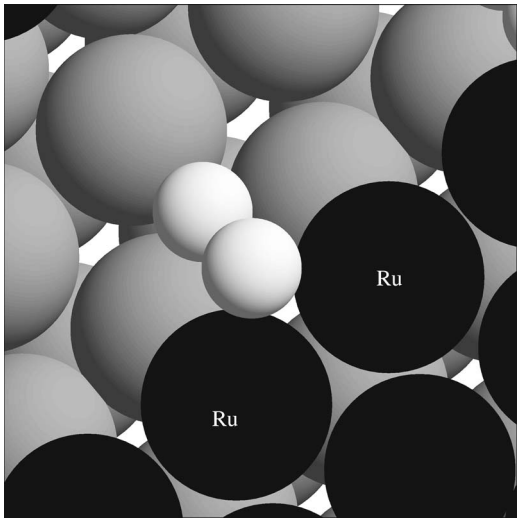

FIG. 1. The transition state for dissociation of N_2. The big and small balls represent Ru and N atoms, respectively. The marked Ru atoms are the two surface atoms whose vibrations are included in the relaxed/N_2+2Ru model.

and modes 6–11 mainly involve motion of the Ru atoms. By comparing the frequencies of the relaxed/N_2 and relaxed/N_2+2Ru models we can conclude that the small differences in frequencies are probably due to the coupling between nitrogen and ruthenium degrees of freedom in the relaxed/N_2+2Ru model.

The surface vibrations do not change the vibrationally adiabatic barrier height significantly, as can be seen in Table I. The coupling changes only the factor $Q^{\ddagger}/Q_{\text{reactants}}$ and therefore has only a small effect on the sticking probability. The thermal sticking coefficients are presented in Fig. 2. The results of the two models considered differ by less than 10%.

TABLE I. DFT results: the classical and vibrationally adiabatic barrier height and harmonic frequencies at the transition state and of the reactants [isolated $N_2(g)$ and 2 Ru atoms].

	Transition state		
	Relaxed/N_2+2Ru	Relaxed/N_2	Frozen
Classical barrier	0.648 eV	0.648 eV	0.999 eV
ΔE	0.641 eV	0.641 eV	0.992 eV
Imaginary frequency	484 i cm^{-1}	483 i cm^{-1}	409 i cm^{-1}
ω_1 (mode 1)	594 cm^{-1}	564 cm^{-1}	578 cm^{-1}
ω_2 (mode 2)	514 cm^{-1}	512 cm^{-1}	517 cm^{-1}
ω_3 (mode 3)	469 cm^{-1}	466 cm^{-1}	446 cm^{-1}
ω_4 (mode 4)	447 cm^{-1}	437 cm^{-1}	423 cm^{-1}
ω_5 (mode 5)	403 cm^{-1}	402 cm^{-1}	411 cm^{-1}
ω_6 (mode 6)	193 cm^{-1}		
ω_7 (mode 7)	183 cm^{-1}		
ω_8 (mode 8)	180 cm^{-1}		
ω_9 (mode 9)	159 cm^{-1}		
ω_{10} (mode 10)	152 cm^{-1}		
ω_{11} (mode 11)	119 cm^{-1}		
	Isolated N_2		
Geometry	2.11a_0	ω	2492 cm^{-1}
	Isolated surface (2Ru atoms)		
$\omega_1 \ldots \omega_6$	207, 192, 188, 148, 140, and 139 cm^{-1}		

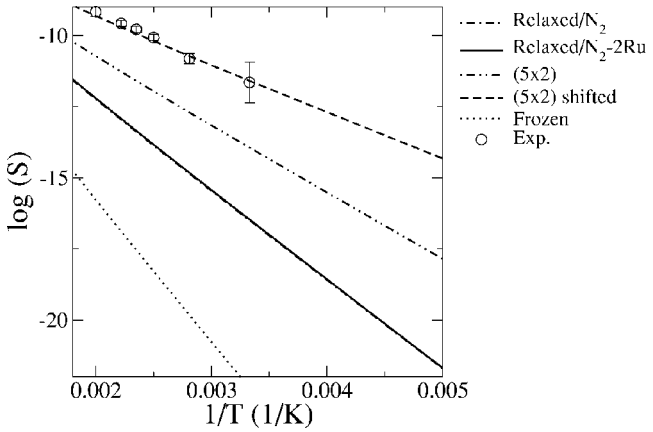

FIG. 2. Arrhenius plot of the thermal sticking coefficient obtained from harmonic TST calculations employing different models. The circles are the experimental results of Dahl *et al.* (Ref. 3).

This suggests that the relaxed/N_2 model, which only takes relaxation of the surface into account but neglects Ru frequencies explicitly, can be used to reliably predict the sticking probability or rate constant.

Figure 2 shows that the sticking coefficient obtained using the relaxed surface models with an activation energy of 0.65 eV is two to four orders of magnitude smaller than the experimental result of Dahl *et al.*[3] Previous work shows[5] that the tunneling is very small and can therefore not explain the observed discrepancy between theory and experiment. However, the dependence of the barrier height on the size of the unit cell partially explains the discrepancy. With a larger (5×2) unit cell (the upper terrace is one atom row broader),[2] employing the relaxed/N_2 model, we obtain a barrier of only 0.49 eV.[2] Using the (5×2) unit cell improves the agreement with the experiment considerably (see Fig. 2). If we lower the classical barrier further down to 0.35 eV, an absolute agreement between theory and experiment is achieved, as shown in Fig. 2. This suggests that in reality the barrier is around 0.35 eV, which agrees very well with the value measured by Dahl *et al.*[4] An error of 0.14 eV for the barrier height is typical for DFT calculations on molecule-surface systems.

The present results also provide an *a posteriori* justification of the frozen surface approximation in previous work,[5] where the contribution of the tunneling effect to the reaction rate was studied. Our justification is based on the following two arguments. First, the normal-mode analysis for the relaxed surfaces models suggests that the coupling between nitrogen and ruthenium degrees of freedom is small at the transition state. Second, the small differences between the transition state harmonic frequencies for the frozen surface model and the relaxed/N_2 model (see Table I) indicate that relaxation of the surface atoms has a small effect on the local shape of the potential around the transition state. In particular, the imaginary frequency changes by less than 20%. As discussed in Ref. 5, the tunneling effect is mainly determined by the imaginary frequency ω_i and is adequately described by the Wigner tunneling theory.[12] According to this theory, the ratio between the rate constants with and without tunneling is given by the tunneling factor $\kappa=1+\frac{1}{24}(\hbar|\omega_i|/k_BT)^2$.[12]

For example, at room temperature (300 K), the tunneling factors are 1.16 and 1.22 for the frozen and relaxed surface models, respectively. Although the tunneling effect is somewhat stronger for the relaxed surface, it still has a marginal effect on the rate constant. At temperatures relevant to ammonia synthesis, the difference is even less: at 750 K κ is 1.03 and 1.04 for the frozen and relaxed surface models, respectively. The effect of surface relaxation is thus predominantly an energy shift. Due to this energy shift the frozen surface model cannot yield quantitative reaction rates, as is clearly demonstrated in Fig. 1. However, the quantum dynamics at the transition state region is correctly described in the frozen surface model.

The present work shows that the effects of surface motion are adequately accounted for in the relaxed/N_2 model. In a previous study we have shown that tunneling effects are negligible.[5] Thus, harmonic TST employing the relaxed/N_2 model is an accurate approach to calculate the rate constants from DFT data. The applicability of this model in first-principles study of the ammonia synthesis rate[2] is therefore confirmed by the present results. The main source of error are the DFT calculations itself. Fortunately, the results of the overall ammonia production are quite insensitive to the DFT errors due to the compensation effect.[13]

The work is financially supported by the European Commission through the RTN Program Predicting Catalysis (HPRN-CT-2002-00170), the Deutsche Forschungsgemeinschaft, and by the Fond der Chemischen Industrie. One of the authors (K.H.) acknowledges the computer resources from the Danish Center for Scientific Computing.

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